[Contribution from the Chemical Laboratory of the University of Michigan]

AN INTERFEROMETRIC INVESTIGATION OF ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS[1]

By F. E. Bartell and C. K. Sloan[2]

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Measurements which have been carried out for the purpose of relating the change in concentration to adsorption have, in practically all cases, been made by means of volumetric or gravimetric methods. Surprisingly few of the investigators have made use of the measurement of refractive index. In the present investigation a Rayleigh interferometer (made by Hilger) was used. Standard methods were employed for the purification of liquids.

For one who is attempting to master the technique of the interferometric method as applied to liquids the papers of Adams,[3] Cohen and Bruins,[4] and Barth and Schaum[5] are of great value. Mitchell[6] and Macy[7] have recently described the use of the instrument for the measurement of the concentration of very dilute aqueous solutions. Others have found interferometry useful in adsorption problems. Odén and Anderson[8] used the interferometer to study the adsorption of the cations of alkali and alkaline earth materials by carbon. In like manner, Ruff[9] determined the amount of phenol adsorbed from solution by a number of commercial carbons. Oliphant and Burdon[10] used the interferometer to measure adsorption of gas on mercury droplets. Others who have made use of interferometry in the study of adsorption from solution include Marc,[11] Wolff,[12] Arendt[13] (who studied the velocity of adsorption by this method), Berl and Wachendorff,[14] and Patrick and Jones.[15]

Preparation and Properties of Carbon.—Bartell and Miller[16] have

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[1] The material presented in this paper is from a dissertation submitted by C. K. Sloan to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928.

[2] DuPont Fellow in Chemistry, 1927–1928.

[3] Adams, This Journal, **37**, 481, 1181 (1915).

[4] Cohen and Bruins, *Z. physik. Chem.*, **103**, 337 (1923).

[5] Barth and Schaum, *Z. wiss. Phot.*, **24**, 145, 158, 166 (1926).

[6] Mitchell, *J. Chem. Soc.*, **129**, 1333 (1926).

[7] Macy, This Journal, **49**, 3070 (1927).

[8] Odén and Anderson, *J. Phys. Chem.*, **25**, 311 (1921).

[9] Ruff, *Kolloid-Z.*, **38**, 59 (1926).

[10] Oliphant and Burdon, *Nature*, **120**, 584 (1927).

[11] Marc, *Z. physik. Chem.*, **81**, 641 (1913).

[12] Wolff, *Kolloid-Z.*, **32**, 17 (1923).

[13] Arendt, *Kolloid Chem. Beihefte*, **7**, 212 (1915).

[14] Berl and Wachendorff, *Kolloid-Z.*, **36**, 36 (1925).

[15] Patrick and Jones, *J. Phys. Chem.*, **29**, 1 (1925).

[16] Bartell and Miller, This Journal, **44**, 1866 (1922).

emphasized the importance of the use of pure carbon in adsorption experiments. They worked out a method for the activation of charcoal prepared by the carbonization of recrystallized sugar. This method, with but slight modification, was used for the preparation of a pure active carbon. The activity of the carbon was tested according to directions given by Miller.[17] It was found that a quarter of a gram of carbon was capable of removing 54% of the benzoic acid from 100 cc. of a 0.02 N solution during ten minutes of intermittent shaking. Miller states that a fairly active carbon will adsorb 50% of the benzoic acid under these conditions. It is possible to prepare a more active carbon but this involves a greater loss in carbon due to oxidation. For the present work it was thought advisable to limit the activation treatment to four hours. A sufficiently active carbon can be obtained during that period without too greatly cutting down the yield. One hundred grams of Merck's saccharose will give about twelve grams of char. Heating this char in nitrogen at 900° reduces the amount to nine grams. The four-hour intermittent activation leaves about five grams of active carbon. After a sufficient quantity is obtained, it should be heated to drive off adsorbed moisture and then kept in a desiccator. It was found that the carbon which had been used for the adsorption of volatile organic liquids can be recovered without changing its adsorptive capacity appreciably.

Modification of Apparatus.—Activated carbon was added to different aqueous solutions of such substances as pyridine, aniline, benzene and a number of acids and alcohols. After a small amount of activated carbon had been added to a saturated solution of benzene in water, the interferometer indicated that all of the benzene had been adsorbed. In each of the other cases a pronounced adsorption of solute occurred. Because of the very slight solubility of many of these substances in water, it was thought desirable to study adsorption from a non-aqueous solvent. The interferometer, however, cannot be used without modification for the analysis of such solutions since organic liquids usually have a higher volatility, a higher temperature coefficient of refractivity and a lower heat capacity than water. Unless certain precautions are taken, these factors result in distortion of the interference band system and uncertainty in the instrument reading. Cohen and Bruins[4] found it necessary to keep their interferometer (Zeiss type) in a water thermostat. A brass plug was made to fill all of the space above the liquid in their interferometer cell in order to prevent evaporation and distillation of liquid against the cover plate of the cell. A few attempts at measuring the concentration of non-aqueous solutions made evident the necessity of considering the precautions given by Cohen and Bruins. The compartments of the cell (Fig. 1) of the Hilger interferometer at first were covered with a plane glass plate. In many cases liquid filled the space between the cell and its cover even though great care was taken in filling the compartments. This liquid slowly evaporated. After the entire instrument had been placed in the large air thermostat used for temperature regulation, loss of liquid due to evaporation was still more pronounced because of the greater circulation of air around the cell. A steel cover was designed to fit over the top of the cell, permitting a mercury seal between the glass of the cell and the cover (Figs. 1 and 2). The under side of the latter carries a groove one-sixteenth of an inch wide extending

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[17] Miller, *J. Phys. Chem.*, **30**, 1162 (1926).

around the top of the glass cell and across the center between the two compartments. This groove is one-quarter of an inch deep and when filled with mercury serves as an effective means of preventing evaporation. A small hole at each end of the top of the cover permits filling the grooves with mercury after the cover is in place on the cell. Liquid is introduced into the compartments through two holes extending through the cover. Mercury seals around each of these holes prevent evaporation at these points.

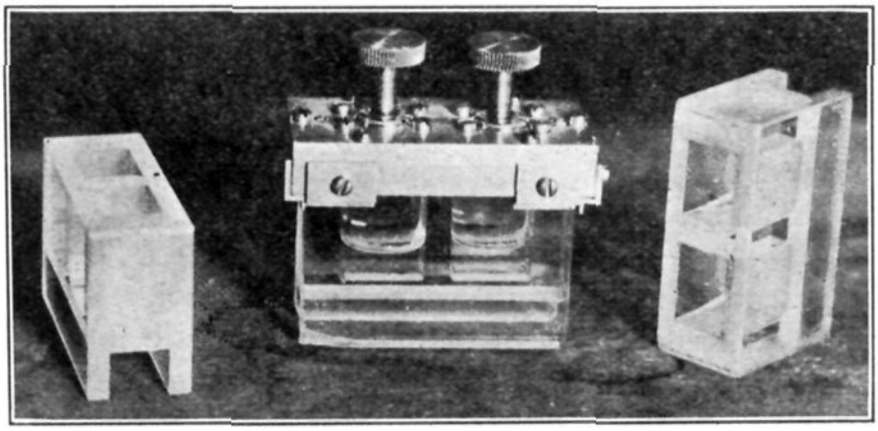

Fig. 1.

Preparation of Solutions and Method of Measurement.—All solutions were made up by weight, the most concentrated being made first and the others obtained by dilution of this with weighed amounts of solvent. The adsorption was carried out in long slender bottles with narrow necks tightly fitted with glass stoppers. The weight of carbon, *m*, was determined by weighing the flask before and after introduction of about a quarter of a gram of carbon. About 5 cc. of solution was then introduced and the increase in weight, *N*, determined. The adsorption bottles were then shaken for twenty hours and put in the air thermostat at 25°. The original solutions were also kept at this temperature for a few hours before making concentration determinations. A portion of the liquid was then removed from the carbon and compared with the original solution in the interferometer cell.

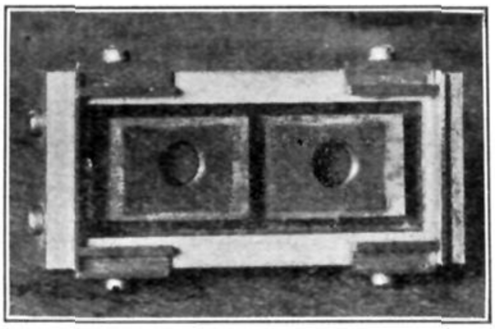

Fig. 2.

The solution of known concentration is always placed in the left-hand compartment of the cell. With this arrangement an interferometer reading greater than the zero reading indicates that the refractive index of the unknown solution is the greater. A calibration is required to determine the difference in concentration corresponding to this reading. This is made by comparing two solutions of known concentration which permits a calculation of the rate of change of concentration with instrument reading (dc/dR). It is highly desirable to compare the solution of unknown concentration with one of nearly the same concentration. If the concentration interval is too great, correction must be made for the change in appearance of the color fringes of the interference system. This phenomenon is fully discussed by Barth and Schaum.[5] A series of calibrations in the range between zero and one per cent. of α-bromonaphthalene in alcohol shows the sensitivity of the method. One division of the interferometer is equivalent to a difference in weight concentration of 0.0000205(dc/dR = 0.0000205). The concentration interval must be equivalent to less than fifty scale divisions; otherwise there may be some difficulty in matching the bands correctly. In many cases adsorption is so great that the equilibrium liquid has to be compared with a solution of known concentration which differs from it less than does the original solution.

Calculation of Data

The Freundlich adsorption equation has been found to apply to the adsorption of solutes when present in low concentration. The degree of adsorption from more concentrated solutions is lower than the equation would indicate. This equation states that the weight of solute removed per gram of adsorbent is proportional to a certain power of the equilibrium concentration of solute. Letting w represent the weight of solute adsorbed by m grams of adsorbent

$$w/m = a'c^n \qquad (1)$$

where c represents the equilibrium concentration of solute and a' and n are constants. The measurement of the refractive index before and after adsorption gives directly the change in concentration of the solution rather than the weight of solute removed. For a small change in concentration of solute due to removal by adsorption, the change (Δc) is directly proportional both to the weight of solute removed (w) and to the concentration of solvent $(1 - c)$, whereas it is inversely proportional to the total amount of solution N. We have, therefore, the relationship

$$\Delta c = a''w(1 - c)/N \qquad (2)$$

Solving for w and substituting in Equation 1 gives

$$N\Delta c/(1 - c)m = ac^n \qquad (3)$$

or

$$N\Delta c/m = ac^n(1 - c) \qquad (4)$$

If we plot a curve from data obtained with the above equation, using $N\Delta c/m$ as one coördinate and c as the other, we find that the first portion of the curve is similar to the ordinary adsorption isotherm. The second term $(1 - c)$, however, soon becomes prominent and causes the curve to pass through a maximum and then decrease to zero when c becomes unity. In this extreme case there would, of course, be no change in concentration even though a maximum of solute were adsorbed. It is evident that the change in concentration at these higher concentrations must be measured very accurately to determine whether the Freundlich equation is applicable. The measurement of refractive index with the interferometer is sufficiently accurate for this purpose.

The adsorption was first expressed in terms of $N\Delta c/m$. In order to compare the adsorption of different substances on a common basis, it was thought desirable to substitute molar units for weight units. Letting x represent the molar concentration, M_1 the gram molecular weight of solute and M_2 the gram molecular weight of solvent, we have

$$x = \frac{1}{1 + M_1(1 - c)/M_2c}$$

Letting H represent the total number of millimoles in solution and Δx the change in molar fraction due to adsorption, it can be shown that

$$H\Delta x/m = (1000x/M_2c)(Nc/m)$$

Results

Some of the results obtained are given in the following tables.

Table I

Adsorption of α-Bromonaphthalene from Ethyl Alcohol[a]

c_0	c	Δc	$N\Delta c/m$	x	$H\Delta x/m$
0.00400	0.00382	0.000178	0.0611	0.0000395	0.1718
.00600	.0056	.000435	.0885	.0000966	.2502
.00800	.00723	.000763	.1157	.0001696	.3255
.01000	.00863	.001367	.1377	.0003037	.3882

[a] The initial and final concentrations are represented by c_0 and c_1, respectively.

Table II

Adsorption of Benzene from Ethyl Alcohol

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.01102	0.2174	0.00236	0.00866	0.0405	0.00513	0.521
.02160	.2327	.00389	.01771	.0611	.01050	0.787
.04335	.2202	.00516	.03819	.0862	.02289	1.123
.08621	.2181	.00661	.07960	.1161	.04854	1.537
.1718	.2170	.00848	.1633	.1473	.1033	2.022

Table III

Adsorption of Ethyl Carbonate from Ethyl Alcohol

c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.00865	0.00042	0.00823	0.010	0.00323	0.084
.01765	.00073	.0170	.015	.00667	.132
.03570	.0014	.0343	.028	.0136	.24
.07178	.0018	.0700	.041	.0286	.360
.1429	.00292	.1400	.061	.0596	.566

Discussion

The foregoing tables and graph indicate that the adsorption by carbon of the three solutes, α-bromonaphthalene, benzene and ethyl carbonate from ethyl alcohol is in accordance with the Freundlich equation ($H\Delta x = ax^n(1 - x)$) for the low concentrations investigated. The constants of the equations representing the adsorption of these substances from dilute alcoholic solution are given in the table below, together with the adhesion-tension[18] value of each against carbon.

Solute	a	n	Adhesion tension
α-Bromonaphthalene	12.1	0.42	89.2
Benzene	9.79	.53	81.1
Ethyl carbonate	4.9	.72	65.6[a]

[a] Unpublished data.

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[18] Bartell and Osterhof, *Z. physik. Chem.*, **130,** 715 (1927); *Ind. Eng. Chem.*, **19,** 1277 (1927).

The order of adsorption from dilute solutions is the same as that of the adhesion tension of the solutes investigated. The coefficient, a, of the Freundlich equation increases in the same order as the adhesion-tension values, while the exponents are in the inverse order. Each of these variations corresponds to an increase in adsorption with increase in adhesion tension. Adhesion tension (A_{12}) is defined as the difference between the surface tension (S_1) of the solid and the interfacial tension (S_{12}) existing at the solid–liquid boundary.

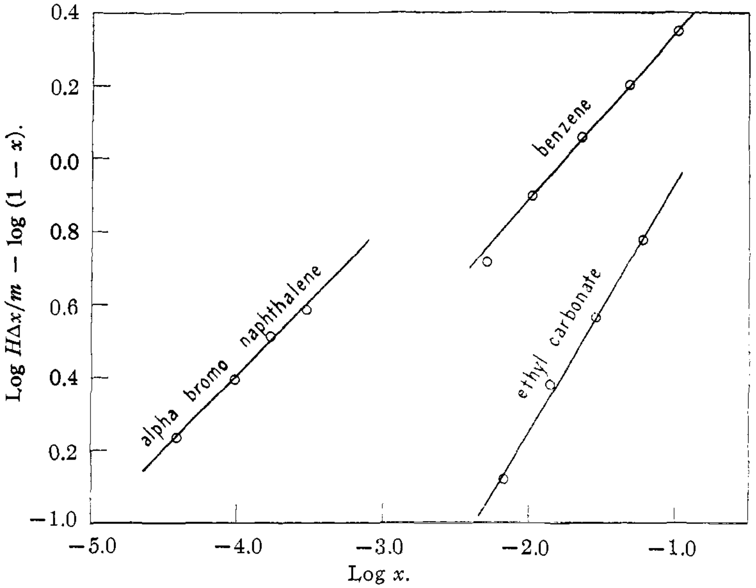

Fig. 3.—Adsorption by carbon from ethyl alcohol.

$$A_{12} = S_1 - S_{12}$$

The adhesion tension, then, is a measure of the decrease in free surface energy which occurs when the solid–liquid interface is substituted for the solid–air interface. It is a measure of the degree to which the solid is wetted by a liquid. The Gibbs principle indicates that greatest adsorption will occur from that system which will produce the greatest lowering of interfacial tension. It may accordingly be reasoned that a liquid which is highly adsorbed by a solid will give a low interfacial tension against that solid. Furthermore, a liquid which with a given solid has a low interfacial tension will in general show a high adhesion tension with it. It is to be expected, then, disregarding solubility effects, that α-bromonaphthalene will be adsorbed to a greater extent from ethyl alcohol than will either benzene or ethyl carbonate because there will be relatively a greater decrease in the free surface energy of the system when α-bromonaphthalene comes in contact with the carbon surface.

Summary

1. The use of the interferometer in measuring the change in concentration due to adsorption from non-aqueous solutions is discussed.

2. Data are given for the adsorption by carbon of α-bromonaphthalene, benzene and ethyl carbonate from dilute solutions in ethyl alcohol.

3. It is pointed out that the adsorption of these solutes by carbon tends to be in the same order as the adhesion-tension values of these same solutes (as pure liquids) against carbon. It is probable that this relationship would obtain in all cases were it not for the influence of other factors such, for example, as solubility of solute with solvent.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE[1]

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Since the accuracy in measurement of change in concentration by the interferometric method is practically independent of concentration, this method was used to study adsorption from non-aqueous systems over the entire concentration range. A series of dilute solutions of ethyl alcohol in benzene was prepared and adsorption by activated carbon measured (Table I) in the manner described in an earlier paper.[3]

TABLE I

ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

Init. alc. concn., $1 - c_0$	m	Δc	$1 - c$	$N\Delta c/m$	x	$H\Delta x/m$
0.01129	0.1777	0.00054	0.01075	0.0118	0.0180	0.255
.02252	.2349	.00098	.02154	.0158	.0359	.337
.04397	.1987	.00101	.04296	.0195	.0806	.412
.08137	.2575	.00067	.08070	.0099	.1294	.203
.15440	.2308	−.00048	.1549	−.0083	.2370	−.164

First, consider the adsorption of benzene when present in relatively small concentration. When the values of log $H\Delta x/m$ are plotted against log x°,[4]

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[1] The material presented in this paper is from a dissertation submitted by C. K. Sloan to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1928. This paper was presented at a meeting of the Colloid Division of the American Chemical Society at Swampscott, September, 1928.

[2] DuPont Fellow in Chemistry, 1927–1928.

[3] Bartell and Sloan, THIS JOURNAL, 51, 1637 (1929).

[4] The symbols used in this paper are the same as those used in an earlier paper: H = total number of millimoles in solution; x = molar concentration; Δx = change in molar concentration; m = weight of adsorbent; c_0 = initial concentration; c = final concentration; N = amount of solution; and a and n are constants.